[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Iodine Pentafluoride–Hydrogen Fluoride System. Solid–Liquid Equilibria, Vapor Pressures, Molar Volumes and Specific Conductances[1]

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Some properties of the iodine pentafluoride–hydrogen fluoride system have been investigated. The solid–liquid phase diagram shows a eutectic point at −83.49° and 99.5 mole % hydrogen fluoride. The vapor pressures at 15° show positive deviations from Raoult's law but no maximum vapor pressure was observed. There is a small decrease in volume on mixing, the maximum deviation from ideality being 6.6% at 90 mole % hydrogen fluoride. The specific conductance of pure iodine pentafluoride at 25° is 5.4×10^{-6} ohm^{-1} cm.$^{-1}$. The specific and molar conductances of mixtures of iodine pentafluoride and hydrogen fluoride have been measured over the entire concentration range.

Introduction

Despite their intrinsic interest and importance the hydrogen fluoride–halogen fluoride systems have been little investigated and no information is available on the iodine pentafluoride–hydrogen fluoride system. We have therefore measured freezing points, vapor pressures, densities and specific conductances of various mixtures of these substances using special equipment for purifying and handling them.

Experimental

Materials.—The apparatus and technique for purification and handling of iodine pentafluoride have been described previously.[2] Freezing point measurements indicated that the impurity content was about 0.0025 molal; the liquid and solid were colorless.

For all but conductance measurements hydrogen fluoride was distilled from a cylinder (Harshaw Chemical Company) and used directly. The observed freezing point (−82.9°) was somewhat higher than that reported in the literature for material of 99.8 mole % purity[3]; our apparatus could not be used for a determination of impurity content by freezing point measurements since the stirrer froze in when only a fraction of the hydrogen fluoride was solid. For conductance work the hydrogen fluoride was passed over cobaltic fluoride to remove water. The specific conductance was about the same as usually used in conductance work,[4] but not as low as the best previously reported values.[5] Our measurements in the regions of high hydrogen fluoride concentration therefore have relative significance only.

Freezing Point Cell.—The cell and stirring arrangement have been described.[2] In this work a glass air-jacket was used which, combined with a transparent Dewar flask, made possible the direct observation of the mixture. No immiscibility in the liquid phase was noted. Temperatures were measured with a calibrated thermocouple; the calibration and the arrangement for recording cooling curves are the same as previously described.[2]

Preparation of Solutions.—The purified halogen fluoride was siphoned directly from a Fluorothene storage container into a weighed Fluorothene tube fitted with a tapered plug and a valve. The line was cleaned by evacuation and heating and the tube, with plug and valve in place, was removed from the vacuum line and weighed on a Torsion Balance. The tube was returned to the line, the contents frozen, and a quantity of hydrogen fluoride allowed to condense in; the valve was then closed and the assembly reweighed. The plug and the valve were then removed and the stirrer assembly (attached to a similar standard taper plug) was inserted. This brief exposure to the atmosphere apparently introduced no appreciable contamination.

For conductance measurements it was found that halogen fluorides siphoned in always had a larger conductance than materials distilled directly into the conductance cell without contacting any metal. For this reason the samples for conductance measurements were made up directly in the conductance cell. The technique was similar to that described above except that the halogen fluoride was distilled into the fluorothene conductance cell.

Concentrations were computed on a mole fraction basis by use of the molecular weight of the monomeric species.

Vapor Pressure Measurements.—Vapor pressures were measured to ±3 mm. by use of a Monel Bourdon Gauge (Helocoid Gauge Division, American Chain and Cable Co.). The gauge was connected directly to the containing vessel but was maintained at a (constant) higher temperature. The temperature of the sample was controlled by a constant temperature bath and stirring was accomplished by a Teflon-covered magnetic stirrer. The movement of the Bourdon tube was measured with a micrometer screw by a method previously described.[6]

Density Measurements.—A pycnometer was constructed by machining a fluorothene bottle with a tapered plug through which the capillary outlet passed. The outlet was attached to a vacuum line and the pycnometer filled by condensing liquid into the cooled tube. The entire assembly was then placed in a thermostat, the level of the liquid in the capillary neck marked, and the assembly removed and weighed. After each such determination the pycnometer was calibrated by filling with pure benzene to the same mark.

Conductance Measurements.—Electrical conductances of the liquids were measured using a Jones-type bridge with tuned oscillator and detector.[7] Measurements were usually made at five fixed frequencies from 400 to 4000 c.p.s. and, if any differences were observed, the data were treated to correct for polarization errors at the smooth platinum electrodes.[7]

A dipping-type cell was constructed entirely of fluorothene except for the smooth platinum electrodes, platinum leads and a copper–constantan thermocouple. The electrodes with their supporting fluorothene framework, the leads, the thermocouple and an inlet tube provided with a valve, were all attached to a male tapered plug which fit into a mating taper in the top of the tube; a clamping device held the assembly together. Fluorothene was used to protect the leads and thermocouple and seal around the places they entered the plug.

Results

Solid–Liquid Equilibria.—The initial and final temperature of solidification obtained from cooling curves are shown in Table I for various mixtures of hydrogen fluoride and iodine pentafluoride. The phase diagram shows only a eutectic point at 99.5 mole % hydrogen fluoride and −83.49°. Although there are rather abrupt changes in slope of the freezing point curve at 5.0 and 48.8 mole % hydrogen fluoride, no definite evidence of a peritectic was

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(1) Physical properties of the halogen fluorides VII. For preceding article in this series see M. T. Rogers, J. G. Malik and J. L. Speirs, THIS JOURNAL, **78**, 46 (1956).

(2) M. T. Rogers, J. L. Speirs, H. B. Thompson and M. B. Panish, *ibid.*, **76**, 4843 (1954).

(3) J. Hu, D. White and H. L. Johnston, *ibid.*, **75**, 1232 (1953).

(4) See, for example, M. Kilpatrick and F. E. Luborsky, *ibid.*, **75**, 577 (1953).

(5) K. Fredenhagen and G. Cadenbach, *Z. anorg. allgem. Chem.*, **178**, 289 (1929).

(6) M. T. Rogers, H. B. Thompson and J. G. Malik, *Rev. Sci. Instr.*, **26**, 730 (1955).

(7) (a) H. B. Thompson, J. L. Speirs and Max T. Rogers, unpublished results; (b) H. B. Thompson and M. T. Rogers, *Rev. Sci. Instr.*, in press.

obtained from the cooling curves. The irregularities might arise from solid-phase transitions but a cooling curve obtained using pure iodine pentafluoride failed to show such a transition.

TABLE I

CRYOSCOPIC DATA FOR IODINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS

Mole % HF	Freezing temp., °C.		Mole % HF	Freezing temp., °C.	
	Initial	Final		Initial	Final
0.00	9.43 ± 0.01	. .	75.50	−20.5	.....
1.99	8.11 ± .02	...	75.70	−20.4	.....
2.06	8.00	...	81.20	−23.2	−83.55
4.51	6.70	...	85.69	−25.9	.....
7.10	4.46	...	86.47	−26.7	−83.59
8.00	4.46	...	90.19	−31.2	−83.49
19.60	− 0.24	...	92.90	−35.1	−83.49
35.60	− 6.00	...	95.59	−44.8	−83.49
47.70	−10.36	−83.4	96.52	−52.0	.....
50.87	−10.90	...	98.5	−72.9	−83.43
55.19	−12.20	...	99.5	−83.49	−83.49
62.87	−15.10	−80 to −85	100	−82.90	.....
70.19	−17.5 ± 0.3	...			

The heat of fusion of iodine pentafluoride obtained from the initial slope of the cooling curve is about 3 kcal./mole. This is in fair agreement with the value 3.6 kcal./mole obtained from the slopes of the vapor pressure curves of pure liquid and solid.[2,8] It was assumed that hydrogen fluoride is a monomeric undissociated solute in making this calculation but the above comparison suggests that some dissociation of the solute may occur. The calculated molal freezing point lowering for iodine pentafluoride dissolved in hydrogen fluoride is 1.53° and the observed is 2.35° which suggests that dissociation may also occur in dilute solutions of iodine pentafluoride in hydrogen fluoride.

Vapor Pressure Data.—The vapor pressures of various mixtures of iodine pentafluoride and hydrogen fluoride are shown as a function of composition in Table II. The observed vapor pressures are higher than computed by Raoult's law from the vapor pressures of the pure substances (using the molecular weights of the monomers to obtain mole fractions), but no azeotrope was observed at this temperature.

TABLE II

THE VAPOR PRESSURES OF IODINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS AT 15°

Mole % HF	p, mm.	Mole % HF	p, mm.
0.0	3	59.1	447
13.4	155	70.5	537
24.5	246	82.6	597
36.2	317	100.0	664

Molar Volumes.—The densities of several mixtures of iodine pentafluoride and hydrogen fluoride were measured to make possible the calculation of molar conductances. The precision of measurement was not great enough to make the calculation of partial molar volumes feasible. However, the average molar volume observed has been compared with that expected for an ideal solution in Table III. There is always a small decrease in volume on mixing, with a maximum difference of about 9%; this may result from the breaking up of the rather open hydrogen-bonded structure of liquid hydrogen fluoride on solution. A small decrease in volume on mixing was also observed in the bromine trifluoride–bromine pentafluoride system.[9]

TABLE III

DENSITIES AND AVERAGE MOLAR VOLUMES OF IODINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS AT 25°

Mole % HF	$d^{25}{}_4$, g./cc.	V_m (av.) obsd.	$V_m{}^0$, ideal	100 $(V_m/V_m)^0$, %
0	3.19	69.5	...	...
56.9	2.64	40.6	42.00	−3.5
89.5	1.72	24.0	26.26	−8.7
93.0	1.51	23.5	24.58	−4.4
100	0.946	21.2	...	...

Conductance Measurements.—Values of the specific conductance of several samples of pure iodine pentafluoride are shown in Table IV. When liquid was transferred directly to the conductance cell from metal apparatus the conductance was always high (run A, $L = 2.4 \times 10^{-5}$ ohm^{-1} cm.$^{-1}$) but when it was distilled directly into the fluorothene cell the conductance was much lower (L = 0.54 to 0.57 $\times 10^{-5}$ ohm^{-1} cm.$^{-1}$ in runs B and C). The latter are lower than previously reported[10,11] values of 2.3×10^{-5} and 1.92×10^{-5}. The spe-

TABLE IV

CONDUCTANCES OF IODINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS AND OF IODINE PENTAFLUORIDE

T, °C.	C, moles HF/l. at 25°	L, ohms^{-1} cm.$^{-1}$ × 10^5	Λ at 25°	Material
25		2.44		IF_5, sample A
25		0.572		IF_5, sample B
25.8		.538		
23.6		.516		IF_5, sample C
17.9		.460		
13.0		.419		
25	0.16	.865	0.02	
22.7	.16	.825		HF in IF_5
19.0	.16	.773		(sample B)
16.6	.16	.739		
25	.061	.662	.015	
25	.083	.724	.018	
25	1.47	1.127	.0038	
25.2	3.75	1.818	.0033	
20.8	3.75	1.706		
16.2	3.75	1.578		
25	7.28	3.21	.0036	HF in IF_5
25	11.3	11.04	.0092	(sample C)
19.9	11.3	11.01		
14.5	11.3	11.03		
24.8	20.6	60.6	.029	
19.5	20.6	60.1		
14.5	20.6	57.5		
25.5	23.7	115	.049	
19.3	23.7	113		
14.9	23.7	111		
25	44	78	.11	
25	45	71	.092	IF_5 in HF
25	48	57	.063	
25	..	29	...	HF alone

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(8) O. Ruff, *Z. angew. Chem.*, **41**, 1289 (1929).

(9) L. Stein and R. C. Vogel, Abstracts of Papers, 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

(10) A. A. Banks, H. J. Emeléus and A. A. Woolf, *J. Chem. Soc.*, 2861 (1949).

(11) H. B. Thompson, Ph.D. Thesis, Michigan State College, 1953.

cific conductance increases linearly with temperature over the range studied.

The conductances of solutions of hydrogen fluoride in iodine pentafluoride also were studied and the results are summarized in Table IV. Both specific and molar conductances decrease at first, then increase, with increase in concentration. Molar conductances are very low in the rather high concentration range studied and hydrogen fluoride must be only slightly ionized in these solutions. The addition of hydrogen fluoride must lead to an actual decrease in the concentration of ionic species present for solutions with hydrogen fluoride concentration between 0.16 and 3.75 molar.

The temperature coefficient of conductance has also been measured at several concentrations (Table IV). The temperature coefficient is positive for each pure component but decreases to zero in a solution with mole fraction hydrogen fluoride about 0.6.

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The 2,2′,2″-Tripyridine System

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The thermodynamic acid dissociation constants for the diacid base 2,2′,2″-tripyridine are $pK_1 = 2.64 \pm 0.07$ for equation 1 and $pK_2 = 4.33 \pm 0.03$ for equation 2. The composite $pK_{1,2}$ is thus 7.0 ± 0.1. The ferrous complex has the formula $FeB_2H_2^{+4}$ and the equilibrium $pK_D = 20.4 \pm 0.2$. Kinetic studies confirm this formula and support the pK_D value in addition to indicating that the ferrous complex is formed through the free base with some form of the ferrous ion involved in the rate-determining step. The work was done at 22–23°.

Compounds containing the —N=C—C=N— linkage have been studied as chelating agents. In particular the complexes of iron(II) with 1,10-phenanthroline[1] and 2,2′-bipyridine[2] have been extensively studied.

2,2′,2″-Tripyridine has received comparatively little study. Brandt and Wright[3] found it to be a diacid base

$$BH_2^{++} \rightleftharpoons BH^+ + H^+ \qquad (1)$$

$$BH^+ \rightleftharpoons B + H^+ \qquad (2)$$

where B = 2,2′,2″-tripyridine. They were able, by potentiometric and conductometric methods, to find a composite $pK_{1,2}$ of 7.1 for the acid dissociation, but were unable to isolate the values for the separate steps. They also found the ferrous complex to contain 2 molecules of tripyridine to one of iron(II) and spectrophotometrically determined the instability constant obtaining an average value of 1×10^{-18}.

In this investigation the acid dissociation constants K_1 and K_2 are isolated, the nature of the ferrous complex elucidated and the kinetics studied for the formation and dissociation of the ferrous complex.

Experimental

Reagents.—2,2′,2″-Tripyridine was obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio. Stock solutions were prepared from the material that was recrystallized from a 40–60° b.p. cut of petroleum ether; m.p. 80–82°.

Stock solutions of iron(II) were prepared from reagent grade hydrated ferrous ammonium sulfate. A small amount of hydroxylamine hydrochloride was added to prevent oxidation.

Reagent grade hydrochloric acid, sodium acetate, sodium hydroxide and sodium mono basic phosphate were used in preparing buffer solutions. Since the latter interferes in the formation of the ferrous complex of the tripyridine[4] it was not used when iron was present.

Instruments.—All absorption measurements were made on a Beckman Model DU Spectrophotometer using matched one centimeter silica or Corex cells. All pH measurements were made on a Cambridge glass electrode pH meter.

Equilibria and Kinetic Studies.—For the formation of the ferrous complex a buffered solution of the tripyridine was prepared in a 50-ml. volumetric flask leaving just sufficient space for the aliquot of iron(II) stock solution. After the addition of the latter the reaction was followed spectrophotometrically until there was no further change in absorption. All solutions were allowed to stand at least 24 hours before measurements were taken for the equilibria studies.

For the studies of the dissociation of the ferrous complex a concentrated solution of the chelate was prepared at a high pH, where little dissociation occurs. Aliquots of this solution were diluted to a sufficiently low pH where considerable dissociation occurs. The dissociation was followed spectrophotometrically until equilibrium was established.

Conditions.—The temperature of all the studies was 22–23°. The final ionic strength of all solutions was 0.10 except in the case of several of the more acid solutions where it was slightly greater.

Results and Discussion

Acid Dissociation Constants.—Figure 1 shows the absorption curves for the various forms of the base. The BH_2^{++} form gave a molar extinction coefficient ϵ_{max} 2.18×10^4 at 288.5 mμ, $p\text{H} < 1.5$ and ϵ_{min} 1.44×10^4 at 281.0 mμ, pH 4.30. For BH^+, ϵ_{max} 1.74×10^4 at 321.5–323.0 mμ, $p\text{H} < 3.0$ and ϵ_{min} 0.60×10^4 at 313 mμ, $p\text{H} > 11.0$. The free tripyridine (B) showed ϵ_{max} 1.60×10^4 at 285 mμ, $p\text{H} > 5.5$.

Plotting total molar extinction coefficient *versus* pH resulted in the usual type curves showing the transition from one form to another.

Let K_2 be the thermodynamic dissociation constant for equation 2. It may be shown that

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[2] J. H. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 57, 736 (1950).

[3] W. W. Brandt and J. P. Wright, THIS JOURNAL, **76**, 3082 (1954).

[4] M. L. Moss and M. G. Mellon, *Anal. Chem.*, **14**, 862 (1942).